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(54) Title: WATER-MODIFIABLE FLUSHABLE POLYOLEFIN-CONTAINING FILM (57) Abstract A water-modifiable polyolefin-containing film having greater than about 55 weight percent of a polyolefin and less than about 45 weight percent of poly(ethylene oxide). Desirably, the polyolefin can be modified by grafting onto the polyolefin from about 0.1 weight percent to about 30 weight percent of a monomer selected from 2-hydroxyethyl methacrylate or polyethylene glycol ethyl ether methacrylate. More desirably, the polyolefin and poly(ethylene oxide) have grafted thereto a total of from about 0.1 weight percent to about 30 weight percent of the monomer. The polyolefin-containing film, when immersed in water for about 30 seconds, will have a loss of a least 10 % in two or more of the tensile properties: percent strain-to-break, peak stress, energy-to-break and modulus when compared to the dry or pre-immersion values.		

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WATER-MODIFIABLE FLUSHABLE POLYOLEFIN-CONTAINING FILM

The application claims priority from the U.S. Provisional Application 60/034,616 filed December 31, 1996, the disclosure of which is incorporated herein by reference.

FIELD OF THE INVENTION

The present invention relates to a flushable polyolefin-containing film. More particularly, the present invention relates to a flushable polyolefin-containing film having greater than about 55 weight percent of a polyolefin and less than about 45 weight percent of poly(ethylene oxide).

BACKGROUND OF THE INVENTION

Personal care products, such as diapers, sanitary napkins, adult incontinence garments, and the like are generally constructed from a number of different components and materials. Such articles typically have some portion, usually the backing layer, liner, or baffle constructed of a liquid repellent film material. This repellent material is appropriately constructed to minimize or prevent the exudation of the absorbed liquid from the article and to obtain greater utilization of the absorbent capacity of the product. The liquid repellent film commonly used includes plastic materials such as polyethylene films and the like.

Although such products are relatively inexpensive, sanitary and easy to use, disposal of a soiled product is not without its problems. With greater interest being placed in protecting the environment today, there is a need to develop materials that are more compatible with the existing and developing waste disposal technologies while still delivering performance consumers have come to expect. An ideal disposal alternative would be to use municipal sewage treatment and private residential septic systems. Products suited for disposal in sewage systems can be flushed down a convenient toilet and are termed "flushable." While flushing such articles would be convenient, the liquid repellent material which normally does not disintegrate in water tends to plug toilets and sewer pipes. It therefore becomes necessary, although undesirable, to separate the barrier film material from the absorbent article prior to flushing.

In addition to the article itself, typically the packaging in which the disposable article is distributed is also made from a water resistant material. Water resistivity is necessary to prevent the degradation of the packaging from environmental conditions and to protect the disposable articles therein. Although this packaging may be safely stored with other refuse for commercial disposal, and especially in the case of individual

packaging of the products, it is often more convenient to dispose of the packaging in the toilet with the discarded disposable article. However, in the cases where such packaging is composed of a water resistant material, plugging of the drains to the toilet typically results.

Desirably, a commercial, flushable product should be relatively responsive to water and be transportable in a sewer system. Commercially available water-soluble polymers, such as polyethylene oxide (PEO), polyvinyl alcohol (PVOH), acrylamide polymers, acrylic acid-based polymers, and cellulose derivatives, possess the desired characteristics for flushability, such as water solubility and/or water dispersibility. However, due to their in-use degradability and storage degradation, these materials function poorly as components in personal care products. Other disadvantages are that these polymers are difficult to process and are substantially more expensive than polyolefins.

The requirements for a functional and flushable product provide a substantial challenge in finding suitable materials with the desired properties. In an attempt to overcome the flushability problem of a water resistant film the prior art has modified the water resistant polymer. One of the more useful ways of modifying polymers involves blending them with other polymers of different structures and properties.

Polymer blends of polyolefins and poly(ethylene oxide) have been shown to be water modifiable at expectedly low weight % polyolefin levels. Such blends would be anticipated to be flushable when exposed to water in a toilet but do not possess the dry mechanical properties required for functionality in use. Moreover, the high content of poly(ethylene oxide) makes such materials prohibitively expensive for use in a disposable personal hygiene article such as a sanitary napkin, diaper and the like. Polymer blends of polyolefins and poly(ethylene oxide) containing greater than about 45 weight percent of polyolefin are generally water resistant and are not water modifiable.

In view of the problems of the prior art, it remains highly desirable to provide a water modifiable film having a substantial portion of thereof composed of a polyolefin. More desirably, the water modifiable film should have greater than about 55 weight percent of a polyolefin. When dry, the film should have the mechanical properties necessary for functionality. When wet, the films should lose at least a portion of its mechanical properties which would render the film flushable and transportable in a sewer system. Such films could be used for making flushable barrier films for personal care products.

SUMMARY OF THE INVENTION

Briefly, the present invention provides for a water-modifiable film or other thermoplastic article having greater than about 55 weight percent of a polyolefin and less than about 45 weight percent of poly(ethylene oxide). As used herein "water modifiable" means that a four mil (one mil equals 0.001 of an inch) thick film, when immersed in water for 30 seconds, will have modified by greater than 10% two or more of the following tensile properties: percent strain-to-break, peak stress, energy-to-break and modulus. To determine the degree of modification, the "wet" values are compared to the pre-immersed or "dry" film values.

Another embodiment of the invention is a water-modifiable film having greater than about 55 weight percent of a modified polyolefin and less than about 45 weight percent of poly(ethylene oxide). The polyolefin is modified by having from about 1 weight percent to about 30 weight percent, based on the total weight of the polyolefin and poly(ethylene oxide), of a monomer grafted onto the polyolefin backbone. Preferably the monomer is 2-hydroxyethyl methacrylate or polyethylene glycol ethyl ether methacrylate.

Another embodiment of the invention is a water modifiable film having greater than about 55 weight percent of a modified polyolefin and less than about 45 weight percent of a modified poly(ethylene oxide). The polyolefin and poly(ethylene oxide) are modified by having a total of from about 1 weight percent to about 30 weight percent, based on the weight of the combined polyolefin and poly(ethylene oxide), of a monomer grafted thereto. Preferably the monomer is 2-hydroxyethyl methacrylate or polyethylene glycol ethyl ether methacrylate.

It is an object of the invention to provide a polyolefin-containing film that is water modifiable. More specifically, it is an object of the invention to provide a polyolefin-containing film having greater than about 55 weight percent of a polyolefin and less than about 45 weight percent of poly(ethylene oxide) that is water-modifiable.

It is another object of the invention to provide a water-modifiable, polyolefin-containing film that when immersed in water for about 30 seconds at least two of the following tensile properties: percent strain-to-break, peak stress, energy-to-break and modulus lose at least 10% of its value relative to the dry film value.

DETAILED DESCRIPTION OF THE INVENTION

Although the present invention is described with reference to a water modifiable film, one skilled in the art would understand the utility of the invention toward other thermoplastic articles that can be extruded or injection molded. In one embodiment of the invention, the water modifiable film comprises greater than about 55 weight percent of a polyolefin and less than about 45 weight percent of poly(ethylene oxide). Desirably, the water-modifiable film comprises from about 55 weight percent to about 85 weight percent of a polyolefin and from about 45 weight percent to about 15 weight percent of poly(ethylene oxide). More desirably, the water-modifiable film comprises from about 65 weight percent to about 85 weight percent of a polyolefin and from about 35 weight percent to about 15 weight percent of poly(ethylene oxide). The poly(ethylene oxide) useful in making the film should have a molecular weight of less than about 200,000 and more preferably about 100,000.

The saturated ethylene polymers useful in the practice of this invention are homopolymers or copolymers of ethylene and polypropylene and are essentially linear in structure. As used herein, the term "saturated" refers to polymers which are fully saturated, but also includes polymers containing up to about 5% unsaturation. The homopolymers of ethylene include those prepared under either low pressure, i.e., linear low density or high density polyethylene, or high pressure, i.e., branched or low density polyethylene. The high density polyethylenes are generally characterized by a density that is about equal to or greater than 0.94 grams per cubic centimeter (g/cc). Generally, the high density polyethylenes useful as the base resin in the present invention have a density ranging from about 0.94 g/cc to about 0.97 g/cc. The polyethylenes can have a melt index, as measured at 2.16 kg and 190°C, ranging from about 0.005 decigrams per minute (dg/min) to 100 dg/min. Desirably, the polyethylene has a melt index of 0.01 dg/min to about 50 dg/min and more desirably of 0.05 dg/min to about 25 dg/min. Alternatively, mixtures of polyethylene can be used as the base resin in producing the graft copolymer compositions, and such mixtures can have a melt index greater than 0.005 dg/min to less than about 100 dg/min.

The low density polyethylene has a density of less than 0.94 g/cc and are usually in the range of 0.91 g/cc to about 0.93 g/cc. The low density polyethylene has a melt index ranging from about 0.05 dg/min to about 100 dg/min and desirably from 0.05 dg/min to about 20 dg/min. Ultra low density polyethylene can be used in accordance with the present invention. Generally, ultra low density polyethylene has a density of less

than 0.90g/cc.

Generally, polypropylene has a semi-crystalline structure having a molecular weight of about 40,000 or more, a density of about 0.90 g/cc, a melting point of 168 to 171°C for isotactic polypropylene and a tensile strength of 5000 psi. Polypropylene can also have other tacticities including syndiotactic and atactic.

The above polyolefins can also be manufactured by using the well known multiple-site Ziegler-Natta catalysts or the more recent single-site metallocene catalysts. The metallocene catalyzed polyolefins have better controlled polymer microstructures than polyolefins manufactured using Ziegler-Natta catalysts, including narrower molecular weight distribution, well controlled chemical composition distribution, co-monomer sequence length distribution, and stereoregularity. Metallocene catalysts are known to polymerize propylene into atactic, isotactic, syndiotactic, isotactic-atactic stereoblock copolymer.

Copolymers of ethylene which can be useful in the present invention may include copolymers of ethylene with one or more additional polymerizable, unsaturated monomers. Examples of such copolymers include, but are not limited to, copolymers of ethylene and alpha olefins (such as propylene, butene, hexene or octene) including linear low density polyethylene, copolymers of ethylene and vinyl esters of linear or branched carboxylic acids having 1-24 carbon atoms such as ethylene-vinyl acetate copolymers, and copolymers of ethylene and acrylic or methacrylic esters of linear, branched or cyclic alkanols having 1-28 carbon atoms. Examples of these latter copolymers include ethylene-alkyl (meth)acrylate copolymers, such as ethylene-methyl acrylate copolymers.

Poly(ethylene oxide) is available from Union Carbide Corporation under the trade name of POLYOX®. Typically, poly(ethylene oxide) is a dry free flowing white powder having a crystalline melting point in the order of about 65°C, above which poly(ethylene oxide) resin becomes thermoplastic and can be formed by molding, extrusion and other methods known in the art.

In another embodiment of the invention, the water-modifiable film comprises greater than about 55 weight percent of a modified polyolefin and less than about 45 weight percent of poly(ethylene oxide). Desirably, the water modifiable film comprises from about 55 weight percent to about 85 weight percent of a modified polyolefin and from about 45 weight percent to about 15 weight percent of poly(ethylene oxide). More desirably, the water-modifiable film comprises from about 65 weight percent to about 85 weight percent of a modified polyolefin and from about 35 weight percent to about 15

weight percent of poly(ethylene oxide). The polyolefin is modified by having grafted thereto from about 0.1 weight percent to about 30 weight percent, based on the weight of the polyolefin and poly(ethylene oxide), of a monomer. Desirably, the polyolefin is modified by having grafted thereto from about 1 weight percent to about 20 weight percent, and more desirably, from about 1 weight percent to about 10 weight percent, based on the weight of the polyolefin and poly(ethylene oxide), of a monomer.

Generally, the modified polyolefin is made by feeding to an extruder an amount of polyolefin, monomer and a free radical initiator. Preferably the monomer is 2-hydroxyethyl methacrylate or polyethylene glycol ethyl ether methacrylate. The modified polyolefin and poly(ethylene oxide) is then melt blended in an extruder to form the water modifiable film. The method of making the modified polyolefin is described in greater detail in copending U.S. patent application 08/733,410 filed October 18, 1996 entitled "METHOD OF MAKING POLYOLEFINS HAVING GREATER THAN 5 PERCENT 2-HYDROXYETHYL METHACRYLATE GRAFTED THERETO", the entire disclosure of which is incorporated herein by reference. In accordance with this embodiment of the invention, suitable poly(ethylene oxide) polymers can have an average molecular weight ranging from 100,000 to about 8,000,000.

The free radical initiators which can be used to graft the monomer onto the polyolefin include acyl peroxides such as benzoyl peroxide; dialkyl; diaryl; or aralkyl peroxides such as di-t-butyl peroxide; dicumyl peroxide; cumyl butyl peroxide; 1,1-di-t-butyl peroxy-3,5,5-trimethylcyclohexane; 2,5-dimethyl-2,5-di(t-butylperoxy) hexane; 2,5-dimethyl-2,5-bis (t-butylperoxy) hexyne-3 and bis(a-t-butyl peroxyisopropylbenzene); peroxyesters such as t-butyl peroxy pivalate; t-butyl peroctoate; t-butyl perbenzoate; 2,5-dimethylhexyl-2,5-di(perbenzoate); t-butyl di(perphthalate); dialkyl peroxy monocarbonates and peroxydicarbonates; hydroperoxides such as t-butyl hydroperoxide, p-methane hydroperoxide, pinane hydroperoxide and cumene hydroperoxide and ketone peroxides such as cyclohexanone peroxide and methyl ethyl ketone peroxide. Azo compounds such as azobisisobutyronitrile may also be used.

In yet another embodiment of the invention a water modifiable film comprises greater than about 55 weight percent of a modified polyolefin and less than about 45 weight percent of modified poly(ethylene oxide). Preferably the water modifiable film comprises from about 55 weight percent to about 85 weight percent of a modified polyolefin and from about 45 weight percent to about 15 weight percent of modified poly(ethylene oxide). More desirably, the water modifiable film comprises from about 65 weight percent to about 85 weight percent of a modified polyolefin and from about 35

weight percent to about 15 weight percent of modified poly(ethylene oxide).

Poly(ethylene oxide) polymers suitable for this embodiment of the present invention can have a molecular weight ranging from 100,000 to 8,000,000. The polyolefin and poly(ethylene oxide) are modified by grafting thereto a total of from about 0.1 weight percent to about 30 weight percent, based on the weight of the polyolefin and poly(ethylene oxide), of the monomer. Desirably, the polyolefin and poly(ethylene oxide) have a total of from about 1 weight percent to about 20 weight percent of the monomer grafted thereto. More desirably, the polyolefin and poly(ethylene oxide) have a total of from about 1 weight percent to about 10 weight percent of the monomer grafted thereto. The water modifiable film of the present invention can be made as described in copending U.S. patent application having U.S. serial no. 08/777,226 filed on December 31, 1996 and entitled "BLENDS OF POLYOLEFIN AND POLY(ETHYLENE OXIDE) AND PROCESS FOR MAKING THE BLENDS", the entire disclosure of which is incorporated herein by reference. Generally, the film is made by melt blending the desired weight ratios of a mixture of the polyolefin, poly(ethylene oxide), the monomer and the free radical initiator in an extruder and at a reaction temperature where the polyolefin and poly(ethylene oxide) are converted to a molten state. Preferably, the polyolefin and poly(ethylene oxide) are added at the beginning of the extruder. After melting, the monomer is added to the melt blend. Further down the extruder barrel, the free radical initiator is fed to the melt blend.

When modifying the polyolefin alone or together with the poly(ethylene oxide), the amount of free radical initiator added to the extruder should be an amount sufficient to graft from about 1 percent to 100 percent of the monomer onto the polymer, i.e., the polyolefin or polyolefin and poly(ethylene oxide). This can range from about 0.1 weight percent to about 2 weight percent of initiator. Preferably, the amount of initiator added to the extruder ranges from about 0.1 weight percent to about 1 weight percent wherein all such ranges are based on the amount of monomer added to the melt blend.

The water-modifiable polyolefin films of the present invention will, when immersed in water for about 30 seconds, have modified at least two of the tensile properties: percent stain-to-break, peak stress, energy-to break and modulus by greater than 10%. Desirably, at least two of the tensile properties will be reduced greater than about 25%. More desirably, at least two of the tensile properties will be reduced from about 25% to about 98%, and even more desirably at least two of the tensile properties: percent stain-to-break, peak stress, energy-to break and modulus will be reduced from about 30% to about 80%. The values in determining the extent of the tensile property or properties

modification are relative to the dry condition, i.e. pre-immersion value for that measured property.

The present invention is illustrated in greater detail by the specific examples presented below. It is to be understood that these examples are illustrative embodiments and are not intended to be limiting of the invention, but rather are to be construed broadly within the scope and content of the appended claims.

COMPARATIVE EXAMPLE A

A 60/40 weight percent blend of low density polyethylene (PE) having a melt index of 1.9 decigrams per minute (dg/min) and a density of 0.917 grams per cubic centimeter (g/cc) (Dow 503I; available from Dow Chemical Company, Midland, MI) and poly(ethylene oxide) (PEO) having a molecular weight of 200,000 g/mol (POLYOX[®] WSRN-80 available from Union Carbide Corp.) was fed to a Haake counter-rotating twin screw extruder at a rate of 5 pounds per hour (lb/hr). The extruder had a length of 300 millimeters. Each conical screw had 30 millimeters diameter at the feed port and a diameter of 20 millimeters at the die. The extruder had four heating zones set at 170, 180, 180 and 190°C. The screw speed of the extruder was 150 rpm.

Film processing of all the blends was performed using a Haake extruder counter-rotating twin screw extruder as described above with the following modifications. The extruder included a 4 inch slit die at a temperature of 195 °C. The screw speed was at 30 rpm. A chilled wind-up roll was used to collect the film. The chilled roll was operated at a speed sufficient to form a film having a thickness of about 4 mils (about 0.004 of an inch) and was maintained at a temperature of 15-20°C.

Dry tensile tests were performed on a Sintech 1/D tensile tester available from MTS Systems Corp., Machesny Park, IL. The film was cut into a type V dogbone shape in accordance with ASTM D638. The test was performed with a grip separation of 30 millimeters and a crosshead speed of 4 millimeters/second.

Wet tensile tests were performed on a Vitrodyne V1000 mini-tensile tester available from Chatillon, Greensboro, NC. The film samples were placed in the grips and the testing apparatus was submerged in ambient temperature, non-stirred water for 30 seconds. The test was then run under the same conditions as the dry tensile test. Peak stress, percent strain-to-break, energy-to-break (as area under stress versus strain curve) and modulus were calculated using the actual stress versus strain values recorded from the tensile tester for each dry or wet tensile test. The peak stress was recorded as the

greatest stress value. The percent stain-to-break was recorded as the percent strain value at break. The energy-to-break (area under stress versus strain curve) was calculated by the summation of rectangular "slices" under the curve determined for each strain value recorded from the tensile test, using the following formula:

$$((\text{Strain value}_x - \text{Strain value}_{x-1}) \times (\text{Stress value}_x + \text{Stress value}_{x-1})) / 2$$

where "x" is the sequential number of the slice. The modulus was calculated by linear regression of the initial region of the stress versus strain curve.

The dry and wet properties of the film produced from the blend in Comparative Example A are indicated in Table 1 below.

TABLE 1

Example #-	#A	
	dry	wet
Thickness (mil)	4.1	4.2
% Strain-to-Break	330	300
Peak Stress - (MPa)	16.6	16.2
Energy-break ($\times 10^6$ J/m ³)	39.4	38.4
Modulus (MPa)	128.4	103.8

% Loss from Dry to Wet	#A
% Strain-to-Break	9%
Peak Stress	2%
Energy-to-Break	3%
Modulus	20%

This example shows typical polymer blends in which the volumetric majority of the blend is water resistant. The polymer blend was not water modifiable after 30 seconds of submersion in water.

EXAMPLES 1-3

For Examples 1-3, the low density polyethylene (Dow 503I) was modified by grafting thereto polyethylene glycol methacrylate (PEG-MA; available from Aldrich

Chemical Company, Milwaukee, WI). A Haake extruder as described in Comparative Example A above was used. The extruder had four heating zones set at 170, 180, 180 and 190°C. The screw speed of the extruder was 150 rpm. The feed to the extruder comprised contemporaneously adding, at the extruder feed throat, 5 lb/hr of polyethylene and the specified amounts of PEG-MA and free radical initiator ((2,5-dimethyl-2,5-di(t-butylperoxy) hexane, supplied by Atochem, 2000 Market St., Philadelphia, PA under the tradename Lupersol 101).

For Example 1 the PEG-MA feed rate was 0.125 lb/hr and the initiator rate was 0.0125 lb/hr.

For Example 2 the PEG-MA feed rate was 0.25 lb/hr and the initiator rate was 0.025 lb/hr.

For Example 3 the PEG-MA feed rate was 0.5 lb/hr and the initiator rate was 0.025 lb/hr.

A 60/40 weight percent blend of polyethylene and poly(ethylene oxide) was prepared following the procedure of Comparative Example A, except the modified polyethylene of each example was substituted for the unmodified polyethylene of Comparative Example A.

The dry and wet properties of the film produced from the blends in Examples 1-3 are indicated in Table 2 below.

TABLE 2

Example #-	#1		#2		#3	
	dry	wet	dry	wet	dry	wet
Thickness (mil)	4.5	4.5	4.0	4.0	5.0	5.0
% Strain-to-Break	330	110	320	70	170	30
Peak Stress - (MPa)	13.8	7.0	11.4	4.9	12.2	3.1
Energy-break ($\times 10^6$ J/m ²)	32.7	6.7	27.6	2.4	16.5	0.5
Modulus (MPa)	117.8	74.4	103.7	56.3	119.4	39.4

% Loss from Dry to Wet	#1	#2	#3
% Strain-to-Break	65%	79%	82%
Peak Stress	49%	57%	75%
Energy-to-Break	80%	91%	97%
Modulus	37%	46%	33%

In accordance with the invention, Examples 1-3 illustrate a water-modifiable film having a modified polyethylene where the polyethylene has PEG-MA grafted thereto and unmodified poly(ethylene oxide). The films were water modifiable after 30 seconds of submersion in water.

Examples 4-7

A 60/40 weight percent resin blend of low density polyethylene, Dow 503I, and poly(ethylene oxide) having a molecular weight of 200,000 g/mol (POLYOX® WSRN-80) was fed to a Haake extruder as described in Comparative Example A at a rate of 5 pounds per hour (lb/hr). Contemporaneously with the polymer feed to the extruder, specified amounts of the monomer, PEG-MA, and free radical initiator (Lupersol 101) were added at the feed throat. The extruder had four heating zones set at 170, 180, 180 and 190°C. The screw speed of the extruder was 150 rpm.

For Example 4 the PEG-MA feed rate was 0.125 lb/hr and the initiator rate was 0.0125 lb/hr.

For Example 5 the PEG-MA feed rate was 0.25 lb/hr and the initiator rate was 0.025 lb/hr.

For Example 6 PEG-MA feed rate was 0.5 lb/hr and the initiator rate was 0.025 lb/hr.

For Example 7 the PEG-MA feed rate was 0.75 lb/hr and the initiator rate was 0.0375 lb/hr.

The dry and wet properties of the film produced from the blends in Examples 4-7 are indicated in Table 3 below.

TABLE 3

Example #-	#4		#5		#6		#7	
	dry	wet	dry	wet	dry	wet	dry	wet
Thickness (mil)	4.4	4.4	5.6	5.5	4.2	4.2	4.9	4.6
%Strain	400	70	280	50	590	90	250	50
Peak Stress - (MPa)	9.3	3.7	8.3	3.1	9.2	3.5	5.2	1.3
Energy-break ($\times 10^6$ J/m ³)	30.6	1.7	18.1	0.9	46.8	2.0	9.8	0.3
Modulus (MPa)	90.1	41.9	91.2	32.7	86.2	38.0	64.4	14.5

% Loss from Dry to Wet	#4	#5	#6	#7
Strain	83%	83%	85%	81%
Peak Stress	60%	63%	62%	75%
Energy-to-Break	94%	95%	96%	97%
Modulus	53%	64%	56%	77%

For Examples 4-7 the amount of monomer grafted to polyethylene was 0.65 weight percent, 1.03 weight percent, 0.51 weight percent and 1.13 weight percent, respectively. The weight percent of monomer grafted to the polyethylene was determined by FT-IR and elemental oxygen content analysis as described in copending U.S. patent application 08/733,410 filed October 18, 1996. For Example 6 the amount of monomer grafted to the poly(ethylene oxide) was determined to be 9.66 weight percent by proton NMR spectroscopy.

In accordance with the invention, Examples 4-7 the water-modifiable films were polymer blends of 60 weight percent of a modified polyethylene and 40 weight percent a modified poly(ethylene oxide) where both the polyethylene and poly(ethylene oxide) have PEG-MA grafted thereto. The films of these polymer blends were water-modifiable after 30 seconds of submersion in water. A dramatic loss in tensile properties was observed for the films from dry to wet.

Examples 8-11

For Examples 8-11, a low density polyethylene, Dow 503I, and poly(ethylene oxide) (WSRN-80) blend was prepared following the procedure of Example 4 having the respective resin weight ratios, PEG-MA feed rates and initiator rates indicated.

For Example 8 the blend was 65/35 PE/PEO, the PEG-MA feed rate was 0.5 lb/hr and the initiator rate was 0.025 lb/hr.

For Example 9 the blend was 70/30 PE/PEO, the PEG-MA feed rate was 0.5 lb/hr and the initiator rate was 0.025 lb/hr.

For Example 10 the blend was 75/25 PE/PEO, the PEG-MA feed rate was 0.5 lb/hr and the initiator rate was 0.025 lb/hr.

For Example 11 the blend was 80/20 PE/PEO, the PEG-MA feed rate was 0.5 lb/hr and the initiator rate was 0.025 lb/hr.

The dry and wet properties of the film produced from the blends in 8-11 are indicated in Table 4 below.

TABLE 4

Example #-	#8		#9		#10		#11	
	dry	wet	dry	wet	dry	wet	dry	wet
Thickness (mil)	5.0	4.8	5.0	5.1	4.6	4.4	4.4	5.2
%Strain	340	80	300	130	260	220	180	150
Peak Stress - (MPa)	7.5	3.6	10.3	5.8	11.3	10.5	11.4	11.4
Energy-break ($\times 10^6$ J/m ³)	21.1	1.6	23.4	6.2	22.8	16.2	16.8	14.7
Modulus (MPa)	91.1	41.0	90.9	55.6	119.9	72.5	138.4	80.6

% Loss from Dry to Wet	#8	#9	#10	#11
Strain	76%	57%	15%	17%
Peak Stress	52%	44%	7%	0%
Energy-to-Break	92%	74%	29%	13%
Modulus	55%	39%	40%	42%

In accordance with the invention, Examples 8-11 were films from polymer blends having greater than about 60 weight percent of a modified polyethylene and less than about 40 weight percent of a modified poly(ethylene oxide) where both the polyethylene and poly(ethylene oxide) have PEG-MA grafted thereto. The films of these polymer blends was water modifiable after 30 seconds of submersion in water. A loss in tensile properties was observed for the films from dry to wet.

Examples 12-15

For Examples 12-15, a 60/40 weight percent resin blend of low density polyethylene (Dow 503I) and poly(ethylene oxide) (WSRN-80) was prepared following the procedure of Example 4, except the monomer used was 2-hydroxyethyl methacrylate. The respective monomer feed rates and initiator rates are indicated.

For Example 12 the 2-hydroxyethyl methacrylate feed rate was 0.125 lb/hr and the initiator rate was 0.0125 lb/hr.

For Example 13 the 2-hydroxyethyl methacrylate feed rate was 0.25 lb/hr and the initiator rate was 0.025 lb/hr.

For Example 14 the 2-hydroxyethyl methacrylate feed rate was 0.5 lb/hr and the initiator rate was 0.025 lb/hr.

For Example 15 the 2-hydroxyethyl methacrylate feed rate was 0.75 lb/hr and the initiator rate was 0.0375 lb/hr.

The dry and wet properties of the film produced from the blends in 12-15 are indicated in Table 5 below.

TABLE 5

Example #-	#12		#13		#14		#15	
	dry	wet	dry	wet	dry	wet	dry	wet
Thickness (mil)	4.5	4.6	4.2	4.7	4.5	4.5	5.0	4.6
%Strain	350	50	390	40	420	40	350	30
Peak Stress - (MPa)	13.3	3.3	9.0	1.5	10.3	2.4	8.7	1.9
Energy-break ($\times 10^6$ J/m ²)	33.3	0.87	26.7	0.36	32.7	0.51	23.6	0.37
Modulus (MPa)	107	38.8	126	18.4	99.6	28.7	109	23.2

% Loss from Dry to Wet	#12	#13	#14	#15
Strain	86%	90%	90%	91%
Peak Stress	75%	83%	77%	78%
Energy-to-Break	97%	99%	98%	98%
Modulus	64%	85%	71%	79%

In accordance with this invention, Examples 12-15 were films of polymer blends having 60 weight percent of a modified polyethylene and 40 weight percent of a modified

poly(ethylene oxide) where both the polyethylene and poly(ethylene oxide) have 2-hydroxyethyl methacrylate grafted thereto. The films of these polymer blends was water-modifiable after 30 seconds of submersion in water.

Example 16

For Examples 16, a Werner & Pfleiderer ZSK-30 extruder (available from Werner & Pfleiderer, Ramsey, New Jersey) was used. The extruder had a pair of co-rotating screws arranged in parallel. The center distance between the two shafts was 26.2 mm. The nominal screw diameter was 30 mm. The actual outer screw diameter was 30 mm. The inner screw diameter was 21.3 mm. The thread depth was 4.7 mm. The extruder had 14 processing barrels, with 13 heated barrels divided into 7 heating zones. The overall processing length was 1340 mm.

A 60/40 weight percent resin blend of low density polyethylene (Dow 503I) and poly(ethylene oxide) having a molecular weight of 100,000 g/mol (POLYOX[®] WSRN-10) was fed to the ZSK-30 extruder at a rate of 35 lb/hr. The seven heating zones were all set at 180 degrees C. The screw speed was 300 rpm.

The dry and wet properties of the film produced from the blend in Example 16 are indicated in Table 6 below.

TABLE 6

Example #-	#16	
	dry	wet
Thickness (mil)	3.2	3.2
%Strain	430	60
Peak Stress - (MPa)	11.3	3.6
Energy-break ($\times 10^6$ J/m ³)	39.5	1.6
Modulus (MPa)	160	45.3

% Loss from Dry to Wet	#16
Strain	86%
Peak Stress	68%
Energy-to-Break	96%
Modulus	72%

In accordance with the invention, Example 16 was a film of a polymer blend of 60 weight percent of an unmodified polyethylene and 40 weight percent an unmodified poly(ethylene oxide). The film of this polymer blend was water modifiable after 30 seconds of submersion in water.

Examples 17-18

For Examples 17-18, a 60/40 weight percent resin blend of low density polyethylene (Dow 503I) and poly(ethylene oxide) having a molecular weight of 200,000 g/mol (POLYOX® WSRN-80) was fed to a ZSK-30 extruder as described in Examples 16 at a rate of 34 lb/hr. The seven heating zones were all set at 180 degrees C. The screw speed was 300 rpm. At barrel 4, the monomer (PEG-MA) was added at the specified rate. At barrel 5, the free radical initiator (Lupersol 101) was added at the specified rate.

For Example 17, the PEG-MA feed rate was 1.02 lb/hr and the initiator rate was 0.068 lb/hr.

For Example 18, the PEG-MA feed rate was 3.06 lb/hr and the initiator rate was 0.17 lb/hr.

The dry and wet properties of the film produced from the blends in Examples 17-18 are indicated in Table 7 below.

TABLE 7

Example #-	#17		#18	
	dry	wet	dry	wet
Thickness (mil)	3.0	4.1	4.2	4.8
%Strain	420	60	310	60
Peak Stress - (MPa)	9.4	1.0	9.1	1.0
Energy-break ($\times 10^6$ J/m ²)	33.9	0.44	24.5	0.37
Modulus (MPa)	85.1	18.6	86.5	25.8

% Loss from Dry to Wet	#17	#18
Strain	86%	81%
Peak Stress	89%	89%
Energy-to-Break	99%	98%
Modulus	78%	70%

In accordance with the invention, Examples 17-18 were films of polymer blends with 60 weight percent of a modified polyethylene and 40 weight percent of a modified poly(ethylene oxide) where both polyethylene and poly(ethylene oxide) have PEG-MA grafted thereto. The films of these polymer blends was water modifiable after 30 seconds of submersion in water.

While the invention has been described with reference to the preferred embodiments and illustrated with regard to a range of optional features, those skilled in the art will appreciate that various substitutions, omissions, changes and modifications may be made without departing from the spirit of the invention. Accordingly, it is intended that the foregoing description be deemed merely exemplary of the preferred scope of the present invention and not be deemed a limitation thereof.

We claim:

1. A water modifiable polyolefin-containing film comprising greater than about 55 weight percent of a polyolefin and less than about 45 weight percent of poly(ethylene oxide) wherein said poly(ethylene oxide) has a molecular weight of less than about 100,000, said film having a loss of at least 10% in two or more tensile properties selected from percent strain-to-break, peak stress, energy-to-break and modulus after being immersed in water for 30 seconds.
2. The film of claim 1 wherein said film comprises from about 55 weight percent to about 85 weight percent of a polyolefin and from about 45 weight percent to about 15 weight percent of poly(ethylene oxide).
3. The film of claim 1 wherein said film comprises from about 65 weight percent to about 85 weight percent of a polyolefin and from about 35 weight percent to about 15 weight percent of poly(ethylene oxide).
4. The film of claim 1, 2 or 3 wherein said polyolefin is polyethylene or polypropylene.
5. The film of claim 1, 2 or 3 wherein said loss in two or more of the tensile properties is greater than 25% after being immersed in water for 30 seconds.
6. The film of claim 1, 2 or 3 wherein said loss in two or more of the tensile properties is from about 25% to about 98% after being immersed in water for 30 seconds.
7. The film of claim 1, 2 or 3 wherein said loss in two or more of the tensile properties is from about 30% to about 80% after being immersed in water for 30 seconds.
8. A polyolefin-containing film comprising greater than about 55 weight percent of a modified polyolefin and less than about 45 weight percent of poly(ethylene oxide) wherein said film has a loss of at least 10% in two or more tensile properties selected from percent strain-to-break, peak stress, energy-to-break and modulus after being immersed in water for 30 seconds.
9. The film of claim 8 wherein said film comprises from about 55 weight percent to about 85 weight percent of a modified polyolefin and from about 45 weight percent to

about 15 weight percent of poly(ethylene oxide).

10. The film of claim 8 wherein said film comprises from about 65 weight percent to about 85 weight percent of a modified polyolefin and from about 35 weight percent to about 15 weight percent of poly(ethylene oxide).

11. The film of claim 8, 9, or 10 wherein said polyolefin is polyethylene or propylene.

12. The film of claim 11 wherein said modified polyolefin has from about 0.1 weight percent to about 30 weight percent of a monomer grafted onto said polyolefin.

13. The film of claim 11 wherein said modified polyolefin has from about 1 weight percent to about 20 weight percent of a monomer grafted onto said polyolefin.

14. The film of claim 11 wherein said modified polyolefin has from about 1 weight percent to about 10 weight percent of a monomer grafted thereto.

15. The film of claim 11 wherein said loss in two or more of the tensile properties is greater than 25% after being immersed in water for 30 seconds.

16. The film of claim 11 wherein said loss in two or more of the tensile properties is from about 25% to about 98% after being immersed in water for 30 seconds

17. The film of claim 11 wherein said loss in two or more of the tensile properties is from about 30% to about 80% after being immersed in water for 30 seconds.

18. The water modifiable polyolefin-containing film of claim 12 wherein said monomer is 2-hydroxyethyl methacrylate or polyethylene glycol ethyl ether methacrylate.

19. A polyolefin-containing film comprising greater than about 55 weight percent of a modified polyolefin and less than about 45 weight percent of a modified poly(ethylene oxide) wherein said film has a loss of at least 10% in two or more tensile properties selected from percent strain-to-break, peak stress, energy-to-break and modulus after being immersed in water for 30 seconds.

20. The film of claim 19 wherein said film comprises from about 55 weight percent to about 85 weight percent of a modified polyolefin and from about 45 weight percent to about 15 weight percent of a modified poly(ethylene oxide).
21. The film of claim 19 wherein said film comprises from about 65 weight percent to about 85 weight percent of a modified polyolefin and from about 35 weight percent to about 15 weight percent of a modified poly(ethylene oxide).
22. The film of claim 19, 20 or 21 wherein said polyolefin is polyethylene or propylene.
23. The film of claim 22 wherein said modified polyolefin and said modified poly(ethylene oxide) have a total of from about 0.1 weight percent to about 30 weight percent of a monomer grafted onto said polyolefin and said poly(ethylene oxide).
24. The film of claim 22 wherein said modified polyolefin and said modified poly(ethylene oxide) have a total of from about 1 weight percent to about 20 weight percent of a monomer grafted onto said polyolefin and said poly(ethylene oxide).
25. The film of claim 22 wherein said modified polyolefin and said modified poly(ethylene oxide) have a total of from about 1 weight percent to about 10 weight percent of a monomer grafted onto said polyolefin and said poly(ethylene oxide).
26. The film of claim 22 wherein said loss in two or more of the tensile properties is greater than 25% after being immersed in water for 30 seconds.
27. The film of claim 22 wherein said loss in two or more of the tensile properties is from about 25% to about 98% after being immersed in water for 30 seconds
28. The film of claim 22 wherein said loss in two or more of the tensile properties is from about 30% to about 80% after being immersed in water for 30 seconds.
29. The water modifiable polyolefin-containing film of claim 23 wherein said monomer is 2-hydroxyethyl methacrylate or polyethylene glycol ethyl ether methacrylate.

INTERNATIONAL SEARCH REPORT

Intr. National Application No PCT/US 97/23810		
A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C08L23/02 C08L51/06		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 C08L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 464 687 A (SHETH PARESH J) 7 November 1995 see abstract	1
A	US 4 415 691 A (ALLEN JAMES A ET AL) 15 November 1983 see abstract	1
A	EP 0 296 355 A (UNION CARBIDE CORP) 28 December 1988 see abstract	1
<input type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family		
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Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Goovaerts, R

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Information on patent family members

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